PATENT APPLICATION

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re application of

Yoshiki SHIRAKAWA, et al.

Appln. No.: 10/535,419

Confirmation No.: 5977

Filed: May 19, 2005

For: POLYESTER MULTIFILAMENT YARN

Docket No: Q87995

Group Art Unit: 1796

Examiner: Gennadiy MESH

SUBMISSION OF SWORN ENGLISH TRANSLATION OF JAPANESE PATENT APPLICATION NO. 2003-077510

Commissioner for Patents
P.O. Box 1450
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Sir:

Submitted herewith is a sworn English Translation of Japanese Patent Application No. 2003-077510.

Respectfully submitted,

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WASHINGTON OFFICE
23373
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Date: April 30, 2008

In re Patent Application of: Yoshiki Shirakawa et al.

Serial No. 10/535,419
Filed: May 19, 2005
For: POLYESTER MULTIFILAMENT YARN

Examiner: MESH, GENNADIY
Group Art Unit: 1796

TRANSLATOR'S DECLARATION

Honorable Commissioner of Patents & Trademarks
Washington, D.C. 20231

Sir:

I, Kazuyuki Nishitate, residing at c/o SEIWA PATENT & LAW, Toranomon 37 Mori Bldg., 3-5-1, Toranomon Minato-ku, Tokyo 105-8423, Japan declare the following:

(1) That I know well both the Japanese and English languages;

(2) That I translated Japanese Patent Application No. 2003-077510, filed March 20, 2003, from the Japanese language to the English language;

(3) That the attached English translation is a true and correct translation of the aforesaid Japanese Patent Application No. 2003-077510 to the best of my knowledge and belief; and

(4) That all statements made of my own knowledge are true and that all statements made on information and belief are believed to be true, and further that these statements are made with the knowledge that willful false statements and the like are punishable by fine or imprisonment, or both, under 18 U.S.C. 1001, and that such false statements may jeopardize the validity of the application or any patent issuing thereon.

April 15, 2008
Date

Kazuyuki Nishitate
Translator Kazuyuki Nishitate

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[REFERENCE NUMBER] P36751

[DATE FILED] March 20, 2003

[DESTINATION] To Commissioner, Patent Office

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[INDICATION OF FEES TO BE PAID]
[Registration Number for Prepayment] 010250
[Amount of Fee] 21,000 yen

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[Name of Article] Specification 1
[Name of Article] Abstract 1
[Number of General Authorization] 0203001
[NEED FOR PROOF] Yes

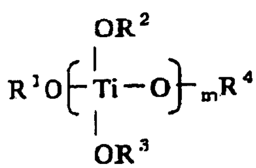
[NAME OF DOCUMENT] SPECIFICATION

[TITLE OF THE INVENTION] POLYESTER FIBER

[SCOPE OF CLAIM FOR PATENT]

[CLAIM 1] A polyester fiber comprising a polyester polymer, wherein an individual filament thickness is from 0.3 to 2.0 dtex, a total thickness is 90 dtex or less, a silk factor (S.F.) is 22 or more, the polyester polymer is a polymer obtained by polycondensing an aromatic dicarboxylate ester in the presence of a catalyst containing a titanium compound component and a phosphorus compound, the titanium compound component is a component containing at least one member selected from the group consisting of a titanium alkoxides represented by the general formula (I):

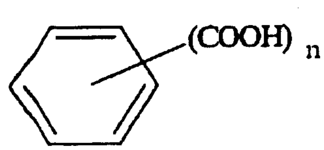
[Chemical 1]



(I)

in which formula (I), R^1, R^2, R^3 and R^4 respectively the same as each other or different from each other and represent an alkyl group or a phenyl group, m represent an integer of 1 to 4, and when m represents an integer of 2, 3 or 4, the 2, 3 or 4 R^2s and R^3s may be respectively the same as each other or different from each other, and a product obtained by reacting the titanium alkoxide represented by the above general formula (I) with an aromatic polyhydric carboxylic acid represented by the general formula (II):

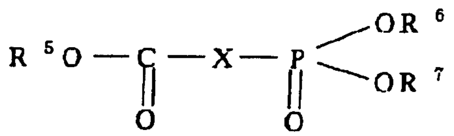
[Chemical 2]



(II)

in which formula (II), n represents an integer of 2 to 4, or an anhydride thereof, and the phosphorus compound is a compound represented by the general formula (III):

[Chemical 3]



(III)

in which formula (III), R^5, R^6 and R^7 respectively the same as each other or different from each other and represent an alkyl group having 1 to 4 carbon atoms, and X represents a $-CH_2-$ or $-CH(Y)$ (wherein Y represents a benzene ring), and the contents of titanium and phosphorus simultaneously satisfy the requirements (1) and (2):

[Numerical 1]

$$1 \leq M_p/M_{Ti} \leq 15 \qquad (1)$$

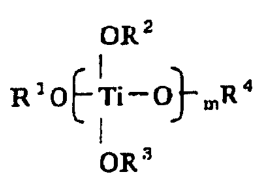
and

$$10 \leq M_p + M_{Ti} \leq 100 \qquad (2)$$

wherein M_{Ti} represents a ratio in % of a value in millimoles of titanium element contained in the polyester to a value in millimoles of the aromatic dicarboxylic acid component, and M_p represents a ratio in % of a value in millimoles of phosphorus element contained in the polyester to the value in millimoles of the aromatic dicarboxylic acid component.

[CLAIM 2] The polyester fiber as claimed in claim 1, wherein the aromatic dicarboxylate ester is a diester obtained by a transesterification reaction of a dialkyl ester of an aromatic dicarboxylic acid with an aliphatic glycol, and the titanium compound component is a component containing at least one member selected from the group consisting of a titanium alkoxide represented by the following general formula (I):

[Chemical 4]

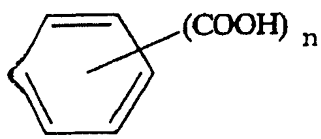


(I)

in which formula (I), R^1, R^2, R^3 and R^4 respectively the same as each other or different from each other and represent an alkyl

group or a phenyl group, m represent an integer of 1 to 4, and when m represents an integer of 2, 3 or 4, the 2, 3 or 4 R^2s and R^3s may be respectively the same as each other or different from each other, and a product obtained by reacting the titanium alkoxide represented by the above general formula (I) with an aromatic polyhydric carboxylic acid represented by the general formula (II):

[Chemical 5]



(II)

in which formula (II), n represents an integer of 2 to 4, or an anhydride thereof.

[CLAIM 3] The polyester fiber as claimed in claim 1 or 2, wherein the polyester is polyethylene terephthalate.

[DETALED DESCRIPTION OF THE INVENTION]

[0001]

[Technical Field of the Invention]

The present invention relates to a polyester fiber. More particularly, the present invention relates to a polyester fiber which is useful for forming a woven and knitted fabric having a good hand and a high mechanical strength, and also has a high resistance to fuzzing and a good color tone.

[0002]

[Prior Art]

Heretofore, polyamide fibers such as nylon 6 and nylon 66 fibers having a high mechanical strength have widely been used in the fields of high strength yarns for clothes. However, polyamide fibers are usually inferior in light resistance as compared with polyester fibers and are therefore required to have high performances in the fields of outdoor sport wears. In the fields of industrial clothes and sport clothes, a higher-order processed article is required to have a low thickness and a high compactibility and an improved hand, and

also raw yarns and woven and knitted fabrics are required to have a high mechanical strength and a small thickness.

[0003]

Each of the polyester polymers constituting fibers for clothes, for example polyethylene terephthalate, is usually produced by directly transesterifying terephthalic acid with ethylene glycol, or transesterifying a lower alkyl ester of terephthalic acid, such as dimethyl terephthalate with ethylene glycol, or reacting terephthalic acid with ethylene oxide to prepare an ethylene glycol ester of terephthalic acid and/or an oligomer thereof, and then polycondensation-reacting the ester monomer or oligomer in the presence of a polycondensation catalyst under a reduced pressure while heating the reaction system until a desired degree of polymerization of the resultant polyester resin is attained. Polyethylene naphthalate, polytrimethylene terephthalate and polytetramethylene terephthalate can also be produced by procedures similar to the above-mentioned procedure.

[0004]

With respect to the procedure, it is well known that the quality of the resultant polyester is greatly influenced by the type of the catalysts used in the polycondensation reaction and, as a polycondensation catalyst for polyethylene terephthalate, antimony compounds are most widely employed since they have excellent polycondensation catalyst performance and a polyester having a good color tone is obtained.

[0005]

However, when an antimony compound is used as the polycondensation catalyst, there arises the following problem. That is, when the resulting polyester is continuously melt-spun for a long time, around a spinneret for melt spinning, foreign matter (hereinafter sometimes referred to as spinneret foreign matter) is deposited thereby to cause a bending phenomenon of a molten polymer stream extruded through the spinneret, which leads to the occurrence of fuzzing and/or breakage of fibers or

yarns or to the unevenness in performances of the fibers or yarns during the spinning step and/or the drawing step. Particularly, it is very difficult to produce fibers required to have a high mechanical strength and a small thickness, and there arises a problem that the production process becomes unstable due to an influence of a spinneret foreign matter, which leads to the occurrence of breakage of fibers or yarns and/or fuzzing.

[0006]

To solve the problem, it is proposed to use a titanium compound, for example, titanium tetrabutoxide as a polycondensation catalyst other than the antimony compound. When using such a titanium compound, however, the resultant polyester polymer exhibits a low thermal stability and, when melted, the polymer is significantly deteriorated. Therefore the production of polyester filaments having high toughness is difficult. Also, there arises a problem that the resultant polyester is colored yellow, and the resultant fibers exhibit an unsatisfactory color tone.

[0007]

As means for solving the problem, it is disclosed in, for example, Patent Document 1, that a product obtained by reacting a titanium compound with trimellitic acid is used as a catalyst for preparation of a polyester, and in, for example, Patent Document 2, that a product obtained by reacting a titanium compound with a phosphite ester is used as a catalyst for producing a polyester. Although the thermal stability of the melt of the polyester is certainly improved to some extent by this processes, the degree of improvement is insufficient and the resulting polyesters have insufficient color tone. Therefore, a further improvement in the color tone of the polyester is required. Furthermore, Patent Document 3 proposes use of a complex of a titanium compound with a phosphorus compound as a catalyst for the preparation of a polyester. Although this process enables the thermal stability of the melt

of the polyester to be improved to some extent, this process has the problem that the degree of improvement is still insufficient and that the color tone of the resulting polyester must be further improved.

[0008]

[Patent Document 1]

Japanese Examined Patent Publication No. 59-46258

[Patent Document 2]

Japanese Unexamined Patent Publication No. 58-38722

[Patent Document 3]

Japanese Unexamined Patent Publication (Kokai) No. 7-138354

[0009]

[Problems to be Solved by the Invention]

In light of the above prior arts, the present invention has been made and an object of the present invention is to provide a polyester fiber which has a small thickness and an excellent hand and capable of exhibiting, when the yarn is converted to a woven and knitted fabric usable for sport clothes, and also has a high resistance to fuzzing, a good color tone and an excellent quality.

[0010]

[Means for Solving the Problems]

In light of the above prior arts, the present inventors have intensively studied and found that a polyester obtained by polycondensation in the presence of a proper catalyst has a stable filament-forming property in spinning of the above fibers having a small thickness and a high strength woven and knitted fabric having a high mechanical strength and good balance between a mechanical strength and an elongation can be obtained from the polymer and also fibers having a high resistance to fuzzing and an excellent color tone can be obtained.

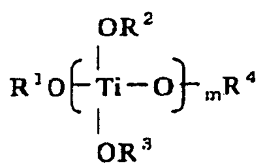
[0011]

Thus, according to the present invention, there is

provided a polyester fiber comprising a polyester polymer, wherein an individual filament thickness is from 0.3 to 2.0 dtex, a total thickness is 90 dtex or less, a silk factor (S.F.) is 22 or more, the polyester polymer is a polymer obtained by polycodensing an aromatic dicarboxylate ester in the presence of a catalyst containing a titanium compound component and a phosphorus compound, the titanium compound component is a component containing at least one member selected from the group consisting of a titanium alkoxide represented by the general formula (I):

[0012]

[Chemical 6]

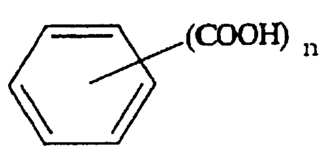


(I)

in which formula (I), R^1, R^2, R^3 and R^4 respectively the same as each other or different from each other and represent an alkyl group or a phenyl group, m represent an integer of 1 to 4, and when m represents an integer of 2, 3 or 4, the 2, 3 or 4 R^2s and R^3s may be respectively the same as each other or different from each other, and a product obtained by reacting the titanium alkoxide represented by the above general formula (I) with an aromatic polyhydric carboxylic acid represented by the general formula (II):

[0013]

[Chemical 7]

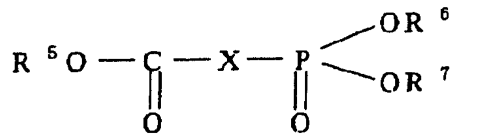


(II)

in which formula (II), n represents an integer of 2 to 4, or an anhydride thereof, and the phosphorus compound is a compound represented by the following general formula (III):

[0014]

[Chemical 8]



(III)

in which formula (III), R^5, R^6 and R^7 respectively the same as each other or different from each other and represent an alkyl group having 1 to 4 carbon atoms, and x represents a $-CH_2-$ or $-CH(Y)$ (wherein Y represents a benzene ring), and the contents of titanium and phosphorus simultaneously satisfy the requirements (1) and (2):

[0015]

[Numerical 2]

$$1 \leq M_p/M_{Ti} \leq 15 \qquad (1)$$

and

$$10 \leq M_p + M_{Ti} \leq 100 \qquad (2)$$

wherein M_{Ti} represents a ratio in % of a value in millimoles of titanium element contained in the polyester to a value in millimoles of the aromatic dicarboxylic acid component, and M_p represents a ratio in % of a value in millimoles of phosphorus element contained in the polyester to the value in millimoles of the aromatic dicarboxylic acid component.

[0016]

[Preferred Mode of the Invention]

The present invention will now be described in detail.

The present invention is directed to polyester fiber comprising a polyester polymer, wherein an individual filament thickness is from 0.3 to 2.0 dtex and a total thickness is 90 dtex or less. In the above fibers, the effect of the present invention can be exerted and also, when an individual filament thickness is from 0.3 to 1.6 dtex and a total thickness is 80 dtex or less, more remarkable effect is exerted. By adjusting the individual filament thickness and the total thickness within the above range, a woven and knitted fabric having a soft hand can be obtained. The fibers with the above

constitution are also suited for a high density woven fabric having an excellent windbreak performance can be obtained. The polyester fibers preferably have 24 or more filaments.

[0017]

In the present invention, it is necessary that the silk factor (hereinafter referred to as S.F., S.F. is represented by Tensile strength × $(\text{Elongation})^{1/2}$ is adjusted to 22 or more. Thereby, the resultant woven and knitted fabric exhibits a high performance in the fields of sport wear and industrial clothes. If the S.F. is less than 22, the target woven and knitted fabric having a high mechanical strength cannot be obtained.

[0018]

In the polyester fibers of the present invention, the mechanical strength is preferably 4.5 CN/dtex or more, and more preferably 4.7 cN/dtex or more. The polyester fibers having a high mechanical strength within the above range enables the resultant woven and knitted fabric to exhibit a high mechanical strength.

[0019]

In the present invention, it is essential that the polyester polymer is a polymer obtained by polycodensing an aromatic dicarboxylate ester in the presence of a catalyst containing a titanium compound component and a phosphorus compound, the titanium compound component is a component containing at least one kind selected from the group consisting of a titanium alkoxide represented by the general formula (I) shown below and a product obtained by reacting the titanium alkoxide represented by the general formula (I) shown below with an aromatic polyhydric carboxylic acid represented by the general formula (II) shown below or an anhydride thereof, and the phosphorus compound is a compound represented by the general formula (III) shown below. Thereby, a woven and knitted fabric having a high mechanical strength can be obtained even in the case of a small thickness, and thus polyester fibers having a high resistance to fuzzing, a good

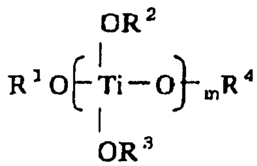
color tone and an excellent quality can be obtained.

[0020]

In view of reducing a foreign matter derived from a catalyst of a final product, it is necessary that the titanate compound component used as a catalyst in the polycondensation reaction is a titanium compound which is soluble in a polymer, and that the titanium compound component is a compound represented by the general formula (I):

[0021]

[Chemical 9]

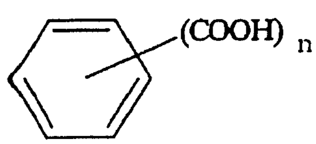


(I)

in which formula (I), R^1, R^2, R^3 and R^4 respectively the same as each other or different from each other and represent an alkyl group or a phenyl group, m represent an integer of 1 to 4, and when m represents an integer of 2, 3 or 4, the 2, 3 or 4 R^2s and R^3s may be respectively the same as each other or different from each other, or a product obtained by reacting the compound represented by the above general formula (I) with a compound represented by the general formula (II):

[0022]

[Chemical 10]



(II)

in which formula (II), n represents an integer of 2 to 4, or an anhydride thereof.

[0023]

Specific examples of the titanium alkoxide represented by the general formula (I), which are preferably used, include titanium tetraisopropoxide, titanium tetrapropoxide, titanium tetra-n-butoxide, titanium tetraethoxide, titanium

tetraphenoxide, octaalkyl trititanate and hexaalkyl dititanate.

[0024]

The aromatic polyhydric carboxylic acid represented by the general formula (II) or the anhydride thereof, to be reacted with the titanium alkoxides are preferably selected from phthalic acid, trimellitic acid, hemimellitic acid, pyromellitic acid and anhydrides of the above-mentioned acids.

[0025]

To react the titanium alkoxide with the aromatic polyhydric carboxylic acid or the anhydride thereof is dissolved in, for example, a solvent; to the resultant mixed liquid, a titanium alkoxide is added dropwise; and the mixture is heated at a temperature of 0 to 200°C for at least 30 minutes, preferably to 30 to 150°C for 40 to 90 minutes. There is no limitation to the reaction pressure, and the reaction pressure may be an ambient atmospheric pressure. The solvent, in which the aromatic polyhydric carboxylic acid or the anhydride thereof, is optionally selected from ethyl alcohol, ethylene glycol, trimethylene glycol, tetramethylene glycol, benzene and xylene.

[0026]

There is no limitation to the molar ratio for the reaction of the titanium alkoxide to the aromatic polyhydric carboxylic acid or the anhydride thereof. However, if the proportion of the titanium alkoxide is too high, the resultant polyester may have a degraded color tone and/or too low a softening point. On the contrary, if the proportion of the titanium alkoxide is too low, the reaction rate of the polycondensation may decrease. Accordingly, the reaction molar ratio of the titanium alkoxide to the aromatic polyhydric carboxylic acid or the anhydride thereof is preferably in the range of from 2/1 to 2/5.

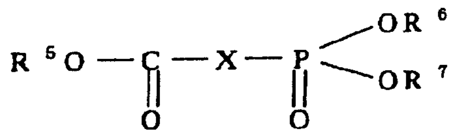
[0027]

In the present invention, the polycondensation catalyst contains the above titanium compound component and a phosphorus

compound represented by the following general formula (III):

[0028]

[Chemical 11]



(III)

in which formula (III), R^5, R^6 and R^7 respectively are the same as each other or different from each other and represent an alkyl group having 1 to 4 carbon atoms, and X represents a $-CH_2-$ or -CH(Y) (wherein Y represents a benzene ring), and is substantially made of an unreacted mixture of both compounds.

[0029]

The phosphorus compound (phosphonate compound) of the above general formula (III) is preferably selected from dimethyl esters, diethyl esters, dipropyl esters and dibutyl esters of phosphonic acid derivatives, for example, carbomethoxymethanephosphonic acid, carboethoxymethanephosphonic acid, carbopropoxymethanephosphonic acid, carbobutoxymethanephosphonic acid, carbomethoxyphenylmethanephosphonic acid, carboethoxyphenylmethanephosphonic acid, carbopropoxyphenylmethanephosphonic acid, and carbobutoxyphenylmethanephosphonic acid.

[0030]

The reaction of the above phosphonate compound with the titanium compound component can proceed at a relatively slow reaction rate compared with a conventional phosphorus compound which is usually used as a conventional stabilizer and, thus, during the polycondensation procedure, the catalytic activity of the titanium compound component can be maintained high for a long time. Therefore, as a result, the amount ratio of the titanium compound component to the polyester can be made low. Also, even if the catalyst system containing the phosphorus

compound of the general formula (III) is added with a large amount of a stabilizer, the thermal stability of the resultant polyester is not decreased and the color tone of the polyester is not affected.

[0031]

In the present invention, it is necessary that the contents of the titanium compound component and the phosphorus compound simultaneously satisfy the following requirements (1) and (2):

[0032]

[Numerical 3]

$$1 \leq M_p/M_{Ti} \leq 15 \qquad (1)$$

and

$$10 \leq M_p + M_{Ti} \leq 100 \qquad (2)$$

wherein M_{Ti} represents a ratio in % of a value in millimoles of titanium element contained in the polyester to a value in millimoles of the aromatic dicarboxylic acid component, and M_p represents a ratio in % of a value in millimoles of phosphorus element contained in the polyester to the value in millimoles of the aromatic dicarboxylic acid component.

[0033]

The ratio M_p/M_{Ti} is preferably 1 or more or but not more than 15, preferably 2 or more but not more than 15, and more preferably not more than 10. If the ratio M_p/M_{Ti} is less than 1, the resultant polyester may have a yellowish color tone, unfavorably. If the ratio is more than 15, the resultant polyester may exhibit an insufficient polycondensation-reactivity, and thus the target polyester may be difficult to produce. The range of the ratio M_p/M_{Ti} is narrower than that of the conventional metal catalyst system. By establishing the ratio M_p/M_{Ti} in the above-mentioned range, an excellent catalytic effect, which has not been obtained in a conventional catalyst system, can be obtained.

[0034]

The sum of $(M_p + M_{Ti})$ is 10 or more but not more than 100,

preferably 20 or more but not more than 70. If the sum of (M_p + M_{Ti}) is less than 10, the production efficiency in the spinning procedure is insufficient, and the resultant fibers exhibit an unsatisfactory performance. Also, if the sum of (M_p + M_{Ti}) is more than 100, the foreign matter derived from the catalyst is accumulated in a small amount, unfavorably.

[0035]

The amount of Ti is preferably from about 2 to 15 millimolar %. The polyester polymer usable for the present invention is a polymer obtained by polycondensing the aromatic dicarboxylate ester in the presence of the catalyst containing a titanium compound component and a phosphorus compound. In the present invention, the aromatic dicarboxylate ester is preferably a diester comprising an aromatic dicarboxylic acid and an aliphatic glycol.

[0036]

The aromatic dicarboxylic acid component preferably comprises, as a principal component, terephthalic acid. More particularly, the terephthalic acid is preferably contained in a content of 70 molar % or more, and more preferably 80 molar % or more, on the basis of the total content of the aromatic dicarboxylic acid component. The preferable aromatic discarboxylic acids other than terephthalic acid include, for example, phthalic acid, isophthalic acid, naphthalenedicarboxylic acid, diphenyldicarboxylic acid and diphenoxyethanedicarboxylic acid.

[0037]

Another aliphatic glycol component is preferably an alkylene glycol, for example, ethylene glycol, trimethylene glycol, propylene glycol, tetramethylene glycol, neopentyl glycol, hexamethylene glycol, dodecamethylene glycol, etc. Among them, ethylene glycol is more preferably employed.

[0038]

In the present invention, the polyester polymer is particularly preferably polyethylene terephthalate. The

polyester is preferably a polyester having, as principal repeating units, ethylene terephthalate groups formed from terephthalic acid and ethylene glycol. In this case, the "principal" repeating ethylene terephthalate unit is contained in a content of 70 molar % or more on the basis of the total molar amount of the repeating units.

[0039]

The polyester polymer usable for the present invention may be a copolyester obtained by copolymerizing a component constituting a polyester as acid components or diol components, in addition to principal repeating units comprising an aromatic dicarboxylic acid and an aliphatic glycol.

[0040]

The component to be copolymerized includes, as the acid component, difunctional carboxylic acids, such as the above-mentioned aromatic dicarboxylic acids, aliphatic dicarboxylic acids, for example, adipic acid, sebasic acid, azelaic acid and decanedicarboxylic acid, and cycloaliphatic dicarboxylic acids, for example, cyclohexanedicarboxylic acid, and ester-forming derivatives of the difunctional carboxylic acids. Also, the diol components to be copolymerized include the above-mentioned aliphatic diols, cycloaliphatic glycols, for example, cyclohexane dimethanol, and aromatic diols, for example, bisphenol, hydroquinone, and 2,2-bis(4-β-hydroxyethoxyphenyl)propanes.

[0041]

Furthermore, copolyesters produced by copolymerizing a copolymerization component comprising polyfunctional compounds, for example, trimesic acid, trimethylolethane, trimethylolpropane, trimethylolmethane and pentaerythriol, can be used.

These copolyesters may be employed alone or in a mixture of two or more thereof.

[0042]

In the present invention, an aromatic dicarboxylate ester

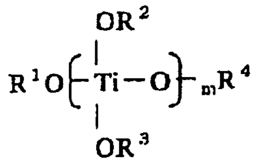
produced from the above-mentioned aromatic dicarboxylic acid and the aliphatic glycol is used. The aromatic dicarboxylate ester can be produced by a diesterification reaction of the aromatic dicarboxylic acid with the aliphatic glycol, or by a transesterification reaction of a dialkylester of the aromatic dicarboxylic acid with an aliphatic glycol. The production of the polyester polymer through the transesterification reaction using, as a starting compound, the dialkyl ester of the aromatic dicarboxylic acid, is advantageous in that the polycondensation procedure can be carried out with less scattering, of the phosphorus compound added as a phosphorus stabilizing agent to the polycondensation system, in comparison with the polycondensation procedure of the aromatic dicarboxylate ester produced by the diesterification reaction of the aromatic dicarboxylic acid.

[0043]

Furthermore, preferably a portion or all of the titanium compound component is preferably mixed with the reaction system before the start of the transesterification reaction, to utilize the titanium compound component as a catalyst for both the transesterification and polycondensation reactions. Thereby, the content of the titanium compound in the polyester can be finally reduced. Examples of polyethylene terephthalate are described in more detail. It is preferred that a transesterification reaction of a dialkyl ester of an aromatic dicarboxylic acid containing terephthalic acid as a principal component with ethylene glycol is carried out in the presence of a titanium compound component containing at least one member selected from a titanium alkoxide represented by the general formula (I):

[0044]

[Chemical 12]

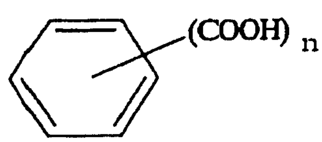


(I)

in which formula (I), R^1, R^2, R^3 and R^4 respectively are the same as each other or different from each other and represent an alkyl group or a phenyl group, m represent an integer of 1 to 4, and when m represents an integer of 2, 3 or 4, the 2, 3 or 4 R^2s and R^3s may be respectively the same as each other or different from each other, and a product obtained by reacting the titanium alkoxide represented by the above general formula (I) with an aromatic polyhydric carboxylic acid represented by the following general formula (II):

[0045]

[Chemical 13]

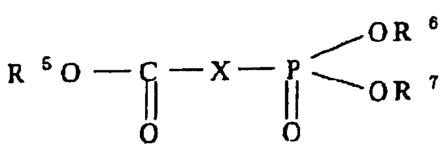


(II)

in which formula (II), n represents an integer of 2 to 4, or an anhydride thereof, and a phosphorus compound represented by the general formula (III):

[0046]

[Chemical 14]



(III)

in which formula (III), R^5, R^6 and R^7 respectively are the same as each other or different from each other and represent an alkyl group having 1 to 4 carbon atoms, and x represents a $-CH_2-$ or $-CH(Y)$ (wherein Y represents a benzene ring), is added to the reaction mixture containing a diester of the aromatic dicarboxylic acid and ethylene glycol, and then the reaction

mixture is polycondensed in the presence of the phosphorus compound.

[0047]

Usually the transesterification reaction is carried out under the ambient atmospheric pressure and, when the reaction is carried out under a pressure of 0.05 to 0.20 MPa, a transesterification reaction due to the catalytic activity of the titanium compound component is further promoted, and the generation of a by-product consisting of diethylene glycol does not occur in a large amount. These effects enable the resultant polyester to exhibit a further improved performance such as, for example, thermal stability. The transeterification reaction is preferably carried out at a temperature of 160 to 260°C.

[0048]

In the present invention, when terephthalic acid is used as an aromatic dicarboxylic acid, the terephthalic acid and dimethyl terephthalate are employed as starting materials for the polyester. In this case, a recycled dimethyl terephthalate obtained by depolymerizing a polyalkylene terephthalate or a recycled terephthalic acid obtained by hydrolyzing the recycled dimethyl terephthalate may be used in a content of 70% or more on the basis of the total content of the acid component in the polyester. In this case, the polyalkylene terephthalate is preferably polyethylene terephthalate. It is preferred to use, as the material source for preparation of a polyester, recovered PET bottles, recovered textile products, recovered polyester film products, and polymer wastes generated in the production processes of these products, in view of the effective utilization of resources.

[0049]

There is no limitation to the method of obtaining dimethyl terephthalate by depolymerizing the recovered polyalkylene terephthalate and any conventionally known method can be employed. Also there is no limitation to the method of

recovering terephthalic acid from dimethyl terephthalate and any conventionally known method can be employed. The total content of impurities contained in terephthalic acid, for example, 4-carboxybenzaldehyde, paratoluic acid, benzoic acid and dimethyl hydroxyterephthalate is preferably 1 ppm or less. The content of monomethyl terephthalate is preferably in the range of from 1 to 5,000 ppm. A polyester can be produced by directly transesterifying the recovered terephthalic acid with an alkylene glycol and polycondensing the resultant ester.

[0050]

The polyester usable in the present invention preferably has an intrinsic viscosity in the range of from 0.64 to 1.00, and more preferably from 0.70 to 0.95. In the case where the intrinsic viscosity is less than 0.64, the resultant fiber may exhibit an insufficient mechanical strength, unfavorably. The intrinsic viscosity is preferably high so as to increase the mechanical strength of the fiber and, when the individual filament thickness is low, the filament-forming property may become difficult. Therefore, the intrinsic viscosity is appropriately controlled according to the target thickness and individual filament thickness. The intrinsic viscosity of the polyester can be optionally controlled by solid phase polymerization.

[0051]

The polyester polymer usable for the present invention optionally contains a small amount of an additive, for example, an antioxidant, an ultraviolet ray-absorber, a flame detardant, a fluorescent brightening agent, a dulling agent, a color tone-controlling agent, a defoaming agent, an antistatic agent, an antibacterial agent, a light stabilizer, a thermal stabilizer and a light-screening agent. Particularly, the polyester polymer is preferably added with titanium dioxide as a dulling agent and an antioxidant as a stabilizer. The titanium dioxide is preferably in the form of particles having an average particle size of 0.01 to 2 μm and is preferably contained in a

content of 0.01 to 10% by mass in the polyester polymer.

[0052]

The antioxidant preferably comprises a hindered phenolic antioxidant. The antioxidant is preferably contained in a content of 1% by weight or less. If the content of the antioxidant is more than 1% by weight, the effect of improving melt stability may be saturated and too high a content of the antioxidant may cause scum to be generated during the melt spinning procedure. The content of the hindered phenolic antioxidant is more preferably in the range of from 0.005 to 0.5% by mass. Also, the hindered phenolic antioxidant may be employed, in combination with a thioether antioxidant, against secondary oxidation.

[0053]

There is no limitation to the method of mixing the antioxidant into the polyester. The mixing procedure may be carried out in any stage between the start of the transesterification reaction and the end of the polycondensation reaction.

[0054]

The polyester fiber, particularly a polyethylene terephthalate-based polyester fiber of the present invention described above can be produced by, for example, the following procedure.

[0055]

First, the polyester polymer chip was melted and extruded through spinning orifices. In this case, the melting temperature is preferably controlled in the range of from 295 to 310°C, and may be appropriately controlled so as to obtain a desired thickness or individual filament thickness. There is no limitation to the profile of the spinning orifices and any spinning orifices having circular, irregular, non-hollow and hollow cross-sectional profiles can be employed.

[0056]

To enhance the filament-forming property and to obtain

higher mechanical strength and elongation, a heater is provided around a hot zone below the spinning spinneret and the atmospheric temperature is controlled to 350°C or higher and results in delayed cooling of the filament. The higher the intrinsic viscosity of the polymer, the more effective. The length of the hot zone is preferably from 40 to 150 mm, and more preferably from 40 to 90 mm. A shutter is provided under the hot zone. Melt streams are usually cooled by a known technique and are cooled by blowing a cooling blast at a temperature of 25°C at a humidity of 65% at a blowing speed of 20 to 40 cm/sec.

[0057]

The melt-spinning speed is preferably 500 to 2,000 m/min. When the melt-spinning procedure is carried out at a speed of more than 2,500 m/min, orientation/crystallization proceeds and thus it is difficult to orient molecules and to attain a high strength.

[0058]

The resultant undrawn filaments are wound-up and then subjected to a drawing procedure or are continuously subjected to the drawing procedure without winding-up. In view of process passing properties, the multifilaments are preferably subjected to a filament-interlacing procedure to impart interlaces between the filaments at a number of interlacing of 1 to 15 interlaces/m before winding-up since sway of the filaments can be suppressed. The draw ratio may be appropriately controlled so as to obtain a desired mechanical strength and elongation.

[0059]

Further, to improve the hand of the polyester fiber of the present invention, a mass-reduction treatment with an alkali is preferably applied to the polyester fiber of the present invention.

[0060]

The polyester fiber of the present invention produced in

the manner as mentioned above can be woven or knitted. The resultant woven and knitted fabrics are preferably utilized in clothes, particularly sport and industrial clothes.

[0061]

[Examples]

The present invention will be further illustrated by the following examples which are not intended to restrict the scope of the present invention in any way.

[0062]

(1) Intrinsic viscosity

An intrinsic viscosity of a polyester polymer was determined from values of the viscosity of an orthochlorophenol solution at 35°C and measured at 35°C in accordance with a conventional method.

[0063]

(2) Color tone (color L* value and color b* value)

A polymer sample was melted at 290°C under vacuum for 10 minutes and was formed, on an aluminum plate, into a plate form having a thickness of 3.0 ± 1.0 mm. The resultant plate-shaped polyester test piece was immediately quenched in iced water, and then subjected to a drying and crystallization treatment at 160°C for one hour. The resultant plate-shaped polyester test piece was placed on a white standard plate for regulating a color-difference meter and Hunter's L* value and b* value of the surface of the plate-shaped polyester test piece was measured by a Hunter's color-difference meter CR-200 manufactured by Minolta Co., Ltd. The L* value means the lightness and the lightness of the test piece increases as the numerical value increases, while the b value represents a yellowness and the yellowness of the test piece increases as the b value increases.

[0064]

(3) Contents of titanium and phosphorus in polyester

A sample of the polyester in the form of particles was heat-melted on an aluminum plate, the polymer melt was formed

into a shaped specimen having a flat surface by using as compression press and the shaped specimen was subjected to an quantitative analysis using a fluorescent X-ray analysis apparatus (model: 3270E, made by RIGAKUDENKIKOGYO K.K.).

[0065]

In the measurement of the titanium concentration of a polymer containing titanium dioxide as a dulling agent, a sample of the polyester was dissolved in hexafluoroisopropanol, the solution was subjected to a centrifugal treatment to cause titanium dioxide particles to deposit, a clear upper liquid fraction of the solution was collected by a decantation method and the solvent was evaporated away from the collected liquid fraction to provide a sample for measurement. The sample was subjected to the analysis.

[0066]

(4) Content of diethylene glycol (DEG)

A sample of the polyester polymer was decomposed with hydrated hydrazine, and the resultant decomposition product was subjected to a gaschromatographic analysis in accordance with a conventional method using a gaschromatograph (model: 263-70, made by K.K. HITACHI SEISAKUSHO) to determine the content of diethylene glycol.

[0067]

(5) Height of foreign matter layer deposited on melt-spinning spinneret

After sinning for 3 days, a maximum height of the layer of a foreign matter deposit formed on an outer periphery of the extrusion hole of the spinneret was measured. The larger the height of the layer of the deposit, the more easily a bending phenomenon of a filament-shaped stream of the extruded polyester melt occurs, resulting in decreased formability of the polyester. That is, the height of the layer of the deposit formed on the spinning spinneret is an index of the formability of the polyester.

[0068]

(6) Formation of fluffs (fluffs/10^6 m)

A multifilament yarn composed of 250 dividual polyester fibers and wound up in the form a package or on a pirn was subjected to a warping procedure using a warping machine equipped with a fluff detecter at a warping speed of 400 m/min for 42 hours. At every step of the warping machine, presence of fluff was checked by the naked eye, and the total number of the fluffs found on the filament yarn per a length of 10^6 m was calculated.

[0069]

[Example 1]

A mixture of 100 parts of dimethyl terephthalate with 70 parts of ethylene glycol was further mixed with 0.009 parts of tetra-n-butyl titanate (TBT). The resultant mixture was placed in a stainless steel reactor having pressurizing means, the pressure of the inside of the reactor was increased to 0.07 MPa and the temperature of the mixture was increased into the range of from 140°C to 240°C, to subject the mixture to a transesterification reaction. Then, the reaction mixture was further mixed with 0.35 parts of triethyl phosphonoacetate (TEPA), and 0.07% by weight of a dulling agent consisting of TiO_2, and then the transesterification reaction was ended.

[0070]

The reaction mixture was moved to a polymerization reactor, heated to a temperature of 290°C, and subjected to a polycondensation reaction under a high vacuum of 26.67 Pa or less. A polyester polymer having an intrinsic viscosity of 0.63 and a diethylene glycol content of 0.6% was obtained. The resultant polyester polymer was formed into polyester polymer chips in accordance with a conventional method. The polyester polymer chips were plaçed in a solid phase polymerization apparatus, and subjected to the polymerization reaction at 220°C for 10 hours. The resultant polyester polymer chips had an intrinsic viscosity of 0.9.

[0071]

Furthermore, the polyester chips were dried and then placed in a melt-spinning apparatus in which the polyester polymer chips were melted and extruded through a melt-spinneret having 36H spinning orifices at an extrusion rate of 15.4 g/min. In this procedure, the temperature of a hot zone located 90 mm below the spinneret was controlled to 400°C by a heater. Toward the extruded filamentary streams of the polyester polymer melt, a cooling blast was blown at temperature of 25°C at a humidity of 65% at a blowing speed of 30 cm/sec., to cool and solidify the melt streams. Then the solidified multifilaments were oiled with an oiling agent by an oiling roller. The oiled multifilaments were subjected to a filament-interlacing procedure to impart interlaces between the filaments at a number of interlacing of 3 interlaces/m. The resultant undrawn multifilament bundle was taken-up at a taking-up speed of 1,000 m/min. and then successively pre-heated at a pre-heating temperature of 90°C without interrupting, and then drawn at a heat-setting temperature of 120°C at a draw ratio of 3.2. The resultant drawn multifilament yarn was wound up at a taking-up speed of 3,200 m/min while, immediately before the taking up, the drawn multifilament yarn was subjected to an interlacing procedure at a number of interlacings of 10 interlaces/m. The resultant drawn multifilament yarn has a yarn count of 44 dtex/36 filaments.

[0072]

The above-mentioned spinning procedure was continuously carried out for 3 days. In the result, no breakage of the yarn occurred. Also, the height of the foreign matter deposit around the spinneret was 5 μm, which was very low. The resultant drawn multifilament yarn exhibited a tensile strength of 4.9 cN/dtex and a silk factor of 23. The number of fluffs generated on the yarn was 0.04 fluffs/10^6 m and thus the yarn exhibited a high fluff-preventing property. The resultant yarn had a very good color tone free from yellowish tone. The

polyester multifilament yarn was converted to a Plain weave having a warp density of 249 warps/3.79 cm and a weft density of 194 wefts/3.79 cm. The resultant Plain weave was subjected to a measurement of tear strength. The determined tear strength was 11.4 N and satisfactory. The resultant woven and knitted fabric had a high softness and exhibited good hand. The test results are shown in Table 1.

[0073]

[Example 2]

The same procedures as in Example 1 were carried out, except that 0.016 parts of titanium trimellitate produced by the method shown below was employed.

Synthesis of titanium trimellitate

A solution of 0.2% of trimellitic anhydride in ethylene glycol was mixed with titanium tetrabutoxide in an amount of 1/2 mole per mole of the trimellitic anhydride, and the resultant mixture was subjected to a reaction by keeping the mixture in the air atmosphere under the ambient atmospheric pressure at a temperature of 80°C for 60 minutes. The reacted mixture was cooled to room temperature. The resultant catalyst was crystallized by using acetone in an amount of 10 times the amount of the mixture, the resultant deposit was separated by a filtration using a filter paper, and the filtered deposit was dried at 100°C for 2 hours to provide a target titanium compound.

[0074]

[Comparative Example 1]

A polyester having an intrinsic viscosity of 0.63 was produced by the same procedures as in Example 1. From the polyester, a drawn filament yarn having a yarn count of 44 dtex/12 filaments was produced by the same procedures as in Example 1 and then from the yarn, a woven and knitted fabric was produced by the same procedures as in Example 1. The resultant woven and knitted fabric had a stiffish hand and thus was unsatisfactory.

[0075]

[Comparative Example 2]

A mixture of 100 parts of dimethyl terephthalate with 70 parts of ethylene glycol and 0.064 parts by weight of calcium acetate monohydrate were charged in a stainless steel container in which a reaction can be effected under pressure, the charged mixture was heated from a temperature of 140°C to a temperature of 240°C under a pressure of 0.07 MPa, to cause a transesterification reaction to occur. The reaction mixture liquid was added with 0.044 parts by weight of an aqueous solution of phosphoric acid in a concentration of 56% by weight, and 0.07% by weight of a dulling agent consisting of TiO_2, to complete the transesterification reaction.

[0076]

Then, the reaction product was moved to a polymerization container and mixed with diantimony trioxide in the amount shown in Table 1, the mixture was heated to a temperature of 290°C and subjected to a polycondensation reaction under a high vacuum of 26.67 Pa or less, to produce a polyester polymer having an intrinsic viscosity of 0.631 and a content of diethylene glycol of 0.55%. The resultant polyester polymer was molded to chips. The polyester polymer chips were then placed in a solid phase polymerization apparatus and subjected to a solid phase polymerization reaction at 220°C for 8 hours. Polyester polymer chips having an intrinsic viscosity of 0.92 were obtained. From the polyester chips, a polyester fiber and a polyester woven and knitted fabric were produced by the same procedures as in Example 1. In the melt-spinning procedure, it was observed that occurrences of breakage of the yarn and the generation of fluffs on the yarn increased with the lapse of the melt-spinning time.

The test results are shown in Table 1.

[0077]

[Table 1]

Table 1

	Ti compound		P compound		Sb compound		M_p/M_{Ti}	$M_p + M_{Ti}$ mmol%	Intrinsic viscosity
	Type	Content mmol%	Type	Content mmol%	Type	Content mmol%			
Example 1	TBT	5	TEPA	30	-	-	6	35	0.900
Example 2	TMT	5	TEPA	30	-	-	6	35	0.900
Comparative Example 1	TBT	5	TEPA	30	-	-	6	35	0.630
Comparative Example 2	-	-	-	-	Sb_2O_3	31	-	-	0.920

Table 1 Continued

	Color tone		Filament-forming characteristics			Fiber characteristics		Characteristics of woven fabric
	B value	L value	Breakage of fibers or yarns	Height of spinneret foreign matter	Fuzzing	Mechanical strength cN/dtex	S.F	Strength N
Example 1	79.0	3.0	0	5	0.04	4.9	23	11.4
Example 2	80.0	2.9	1	6	0.04	4.8	23	11.3
Comparative Example 1	80.0	2.6	0	7	0.03	4.3	21	6.7
Comparative Example 2	70.0	2.8	10	33	0.15	4.7	23	11.1

[0078]

[Effect of the Invention]

According to the present invention, polyester fibers having a high resistance to fuzzing, a good color tone and an extremely excellent quality can be provided. Moreover, a woven and knitted fabric having a high mechanical strength is obtained from the resultant fifers, regardless of a soft and excellent hand of the fibers, and the woven and knitted fabric can be preferably used in the fields of sport wear and industrial clothes.

[NAME OF DOCUMENT] ABSTRACT
[SUMMARY]
[OBJECT] To provide a polyester which has a small thickness and an excellent hand and capable of exhibiting, when the yarn is converted to a woven and knitted fabric usable for sport clothes, and also has a high resistance to fuzzing, a good color tone and an excellent quality.
[SOLUTION MEANS]

A fiber having an individual filament thickness of 0.3 to 2.0 dtex, a total thickness of 90 dtex or less and a silk factor (S.F.) of 22 or more is obtained from a polyester obtained by polycondensing an aromatic dicarboxylate ester in the presence of a catalyst containing a specific titanium compound component and a phosphorus compound.
[SELECTED DRAWING] None